

# Vadose Zone Processes and Chemical Transport

## Aging Effects on Cadmium Transport in Undisturbed Contaminated Sandy Soil Columns

P. Seuntjens,\* K. Tirez, J. Šimůnek, M.Th. van Genuchten, C. Cornelis, and P. Geuzens

### ABSTRACT

Limited information is available on the effects of contaminant aging (i.e., the contact time of Cd with the soil) on Cd transport in soils. We conducted displacement experiments in which indigenous Cd and freshly applied Cd were leached simultaneously from undisturbed samples of three Spodosol horizons. Sorption of Cd was described using Freundlich isotherms, whereas transport was described as a convection–dispersion process. Parameter optimization analysis using a mobile–immobile transport model applied to nonsorbing tracer displacement data showed that 16 to 22% of the water in the columns was immobile. The low dimensionless mass transfer coefficients in the mobile–immobile model were indicative of diffusion-limited transfer between mobile and immobile water, and hence physical nonequilibrium. A two-site kinetic sorption model could be fitted closely to breakthrough curves of the non-aged Cd for three soil horizons. No conclusive evidence was found that contaminant aging in soil affects cadmium transport. On the one hand, predictions of aged Cd leaching, using parameters estimated from displacement experiments with non-aged Cd, differed from those for the aged Cd in the E horizon. On the other hand, no meaningful differences in transport behavior between aged and non-aged Cd were found for the humus Bh and Bh/C horizons. The two-site kinetic rate coefficient  $\alpha_c$  was found to depend on water flux, further indicating that mass transfer between sorption sites and the liquid is limited by diffusion rather than by kinetic sorption.

HEAVY metals are being added to the environment by atmospheric deposition and by fertilizer, sludge, and sewage sludge application to the soil. Specific soil conditions may favor heavy metal migration through the unsaturated zone to underlying aquifers. In the long term, mobile heavy metals may adversely affect drinking water supplies and the quality of surface waters connected to contaminated areas. The physical and chemical mechanisms affecting heavy metal transport and transformations need to be accurately represented in solute transport models in order to correctly predict soil and ground water quality, as well as to evaluate the feasibility of soil cleanup programs.

Because of its mobility in the environment and its harmful effects on humans, the behavior and transport of Cd in soils has been widely studied. For example, Selim et al. (1992) compared the performance of multi-

reaction and multicomponent models to predict Cd transport in soil columns. A competitive equilibrium ion-exchange transport model predicted Cd breakthrough adequately, while a multireaction model with independently measured rate constants largely underestimated the extent of Cd retention. Hinz and Selim (1994) predicted Cd and Zn transport in uniformly packed soil columns under constant and variable ionic strength conditions. They failed to predict Cd transport under constant ionic strength, and from this concluded that not all reactions were accounted for by the adsorption isotherms. An empirical Cd sorption model that included pH and organic matter was proposed by van der Zee and van Riemsdijk (1987) for acid sandy soils. Temminghoff et al. (1995) extended this sorption model to a three-species Freundlich equation that accounted for Ca activity, pH, complexation, and ionic strength of the soil solution. The modified sorption isotherms were derived for a range of sandy soils differing in pH, organic matter content, and soil solution composition. Modified isotherms are especially advantageous in estimating sorption parameters from basic soil information, thus making them useful for large-scale (field and regional) applications.

Relatively little attention has thus far been paid to the transport behavior of *aged* contaminants (i.e., for sorbing solutes that reside for relatively long time periods in the soil, from several years up to tens of years). Such solutes can migrate into less accessible immobile soil water regions and/or may diffuse into and become strongly bound within the soil solid phase. Consequently, the time needed for a contaminant to dissolve or be transferred from stagnant to mobile water may increase. Discussions are still ongoing whether or not irreversible Cd fixation in soils occurs. For example, Christensen (1984b) did not observe irreversible Cd binding to a loamy sand and a sandy loam soil in 0.01 M CaCl<sub>2</sub> at pH = 6. He showed that 67 wk of aging of Cd in the soil did not significantly change Cd desorption. Ainsworth et al. (1994) studied desorption of 16-wk aged Cd on hydrous ferric oxide and observed that 20% did not desorb. Wilkens (1997) found that Cd desorption from sandy soils deviated from adsorption and attributed the difference to sorption hysteresis. Smolders et al. (1999) measured the exchange between radio-labile <sup>109</sup>Cd and indigenous Cd in 10 Belgian soils and found that 62 to 90% of the indigenous Cd was labile (i.e.,

P. Seuntjens, K. Tirez, C. Cornelis, and P. Geuzens, Vito, Flemish Institute for Technological Research, Boeretang 200, B-2400 Mol, Belgium. J. Šimůnek and M.Th. van Genuchten, USDA-ARS, George E. Brown, Jr., Salinity Lab., 450 W. Big Springs Road, Riverside, CA 92507-4617. Received 14 June 2000. \*Corresponding author (piet.seuntjens@vito.be).

**Abbreviations:** 2SF, two-species Freundlich model; 3SF, three-species Freundlich model; BTC, breakthrough curve; CDE, convection–dispersion model; LEA, local equilibrium; TRM, two-region model.

isotopically exchangeable). A decrease in the soil pH increased the labile Cd pool, thus indicating that changes in soil solution composition may cause a release of previously sorbed Cd.

Most Cd transport studies have been carried out using homogeneous saturated soil columns. However, field and laboratory experiments with conservative tracers in undisturbed soils have shown that heterogeneous flow and preferential or nonequilibrium transport conditions often exist in unsaturated soils due to spatial heterogeneity of hydraulic properties, the presence of macropores, flow instabilities, and variable boundary conditions. Studies indicate that preferential solute transport is common in many coarse-textured soils (Glass et al., 1989; Baker and Hillel, 1990; Ritsema et al., 1993; Kung, 1993). Laboratory experiments with undisturbed soil cores or in situ field experiments are useful for studying preferential flow and transport. Büchter et al. (1996) conducted a migration experiment with Cd in an undisturbed stony soil column. They concluded that Cd transport could be well predicted using a convective-dispersive transport model with either a monocomponent isotherm or an ion-exchange isotherm. They observed sorption hysteresis, which they modeled as an irreversible sorption process. Unsaturated conditions as such may also contribute to non-ideal tracer transport (e.g., Biggar and Nielsen, 1960).

Non-ideal reactive solute transport may be described using a bicontinuum concept by dividing the soil into two pore water regions (physical nonequilibrium; van Genuchten and Wierenga, 1976) or two sorption domains (chemical nonequilibrium; Selim et al., 1976). Nonequilibrium is then either assumed to be caused by rate-limited diffusive mass transfer between mobile and immobile water regions, or by kinetic sorption reactions. Nkedi-Kizza et al. (1984) showed that the mathematical formulation of physical and chemical nonequilibrium processes is equivalent and that the two types of nonequilibrium cannot be easily distinguished on the basis of column outflow experiments. Although conceptually more elaborate approaches have been proposed to distinguish between different sources of nonequilibrium (e.g., Brusseau et al., 1989), they seem to be of limited practical importance when evaluating macroscopic solute fluxes.

In this study, we evaluated the ability of two modified Freundlich isotherms to describe sorption of Cd in different horizons of a layered sandy soil. We also compared the leaching behavior of Cd that resided for decades in the soil (i.e., indigenous Cd) with the simultaneous breakthrough curve of a  $^{111}\text{Cd}$  isotope tracer added to the same soil. The indigenous Cd originates from CdO deposition. Under acidifying conditions, CdO has been shown to be readily soluble (Smolders, unpublished data, 1999). This means that both the  $^{111}\text{Cd}$  isotope and the indigenous Cd are added to the soil as a soluble metal salt. In the displacement experiments, they are in the same chemical form (i.e., in part as a divalent cation and in part as soluble chloride complex). The transport behavior of indigenous and tracer Cd can be readily compared.

## MATERIALS AND METHODS

### Cadmium Retention in Soils

Retention of metals in soils can be described by two dominant processes: (i) the metal is sorbed to the soil matrix as a readily exchangeable ion, and (ii) the metal is sorbed with a high affinity to specific sites on the soil matrix (Selim et al., 1992). The second reaction (i.e., specific sorption) causes the metal to be strongly bound to the soil solid phase. This type of reaction includes the formation of inner- and outer-sphere complexes, surface precipitation, and incorporation of heavy metal ions into the mineral lattices of the soil. In acid sandy soils the first process is generally assumed to be predominant since specific sorption of Cd is unlikely to occur (Boekhold and van der Zee, 1992).

Reversible Cd sorption can be modeled using either a macroscopic sorption isotherm describing reversible sorption reactions, or an ion-exchange isotherm describing competition of metal ions for the same exchange sites on the solid phase (e.g., between  $\text{Cd}^{2+}$  and  $\text{Ca}^{2+}$ ). The former isotherm is often used when predicting the retention of reactive solutes under conditions of constant ionic strength and a constant background solution, while the latter isotherm is more appropriate when simulating conditions of variable ionic strength. The sorption isotherm relates the sorbed concentration  $s$  ( $\text{mg kg}^{-1}$ ) to the solution concentration  $c$  ( $\text{mg L}^{-1}$ ). Cadmium sorption is frequently described using a Freundlich sorption isotherm:

$$s = k_f c^{n_{\text{Cd}}} \quad [1]$$

where  $k_f$  ( $\text{mg}^{(1-n)} \text{L}^n \text{kg}^{-1}$ ) and  $n_{\text{Cd}}$  are empirical constants. Based on earlier work by Chardon (1984), van der Zee and van Riemsdijk (1987) proposed an empirical isotherm that considers the effects of pH and organic matter content on sorption. This model is referred to here as the two-species Freundlich (2SF) model because it considers two species in the soil solution ( $\text{H}^+$  and  $\text{Cd}^{2+}$ ):

$$s = k_{2\text{SF}} \cdot \text{OC} \cdot (\text{H}^+)^m c^{n_{\text{Cd}}} \quad [2]$$

where  $k_{2\text{SF}}$  is the 2SF sorption constant ( $\text{mg}^{(1-n)} \text{L}^n \text{kg}^{-1}$ ),  $(\text{H}^+)$  is the proton activity in the soil solution:  $10^{-\text{pH}}$  ( $\text{mol L}^{-3}$ ), OC is the organic matter content (%), and  $m$  and  $n_{\text{Cd}}$  are empirical constants. The exponent  $m$  ( $=-0.5$ ) was derived in other studies (Chardon, 1984) involving sorption experiments at different pHs. The modified Freundlich sorption constant  $k_{2\text{SF}}$  depends on the composition of the soil solution. van der Zee and van Riemsdijk (1987) compiled isotherms from experiments of Chardon (1984) for a variety of soils. They derived a modified sorption constant  $k_{2\text{SF}}$  in Eq. [2] of  $0.048 \text{ mg}^{(1-n)} \text{L}^n \text{kg}^{-1}$ , and a Freundlich exponent  $n$  of 0.85.

From theoretical considerations of sorption onto heterogeneous soil surfaces leading to a non-ideal competitive adsorption (NICA) model (Koopal et al., 1994), Temminghoff et al. (1995) proposed a simplified equation for multicomponent Ca and Cd sorption, referred to as the three-species Freundlich (3SF) model:

$$s = k_{3\text{SF}} \text{OC} \cdot (\text{H}^+)^m \cdot (\text{Ca})^{n_{\text{Ca}}} \cdot (c)^{n_{\text{Cd}}} \quad [3]$$

where  $(c)$  is the Cd activity in the soil solution;  $(\text{Ca})$  is the Ca activity in the soil solution ( $\text{mol L}^{-3}$ );  $k_{3\text{SF}}$  is the modified Freundlich sorption constant ( $\text{mg}^{(1-n)} \text{L}^n \text{kg}^{-1}$ ); and  $n_{\text{Ca}}$  is an empirically derived exponent. The Cd activity in the soil solution is determined by inorganic complexation (e.g., with  $\text{Cl}^-$  and  $\text{NO}_3^-$ ) and by the ionic strength of the soil solution. Cadmium and Ca activities were calculated from, respectively:

$$(c) = c_f c_d F \quad [4]$$

$$(Ca) = [Ca]f_{Ca} \quad [5]$$

with:

$$-\log(f_{Cd/Ca}) = 2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right) \quad [6]$$

and:

$$F = \frac{[Cd^{2+}]}{[Cd_{total}]} = \frac{1}{1 + \sum_q K_q^I [X]^q} \quad [7]$$

where in Eq. [4] and [5],  $f_{Cd}$  and  $f_{Ca}$  are the activity coefficients of Cd and Ca, respectively, and  $F$  is the complexation coefficient. The activity coefficient  $f$  is calculated from the Davies extension of the Debye-Hückel equation (Bolt and Bruggenwert, 1978) represented by Eq. [6], in which  $I$  is the ionic strength. The complexation coefficient  $F$  is calculated from Eq. [7] in which  $K_q^I$  is the formation constant of the Cd complexes with  $X$  at ionic strength  $I$  and  $[X]$  is the Cl concentration. Formation constants of Cl complexes were taken from Sillen and Martell (1971) and Smith and Martell (1981). The sorption isotherm (Eq. [3]) thus explicitly accounts for solution complexation with  $Cl^-$ , competition with Ca, and pH. All remaining processes influencing Cd sorption are lumped into the modified Freundlich constant  $k_{3SF}$ . Temminghoff et al. (1995) found the parameters  $n_{Cd} = 0.85$ ,  $n_{Ca} = -0.34$ ,  $m = -0.69$ , and  $k_{3SF} = 10^{-3.81} \text{ mol}^{(1-n)} \text{ L}^n \text{ kg}^{-1}$  for combined sorption data obtained at various pH levels and ionic strengths.

## Cadmium Transport

### Equilibrium Transport

One-dimensional transport of a sorbing solute through a homogeneous soil at constant water content is described here using the convection-dispersion equation (e.g., Lapidus and Amundson, 1952):

$$\rho \frac{\partial s}{\partial t} + \theta \frac{\partial c}{\partial t} = \theta D \frac{\partial^2 c}{\partial x^2} - J_w \frac{\partial c}{\partial x} \quad [8]$$

where  $t$  is time (d),  $x$  is distance (dm),  $\rho$  is the soil bulk density ( $\text{kg L}^{-1}$ ),  $\theta$  is the soil water content ( $\text{dm}^3 \text{ dm}^{-3}$ ),  $D$  is the dispersion coefficient ( $\text{dm}^2 \text{ dm}^{-1}$ ), and  $J_w$  is the volumetric water flux density ( $\text{dm}^2 \text{ dm}^{-1}$ ). Cadmium sorption is introduced into Eq. [8] using a nonlinear Freundlich isotherm (Eq. [1]). Equation [8] must be solved numerically unless the isotherm is linearized and relatively simple initial and boundary conditions are invoked. The dispersion coefficient  $D$  in Eq. [8] can be determined experimentally by performing a non-reactive tracer experiment at the same flow velocity and measuring its breakthrough curve in the column effluent.

### Nonequilibrium Transport

In many displacement experiments high water fluxes are often used in order to leach strongly sorbing chemicals. These high water fluxes may induce nonequilibrium transport. Two types of nonequilibrium are frequently assumed (i.e., physical and chemical nonequilibrium). The conceptual model describing physical nonequilibrium divides the soil water phase into mobile and immobile (or stagnant) regions. Convective-dispersive transport is confined to the mobile water phase, while transfer of solutes into and out of immobile water is assumed to be diffusion controlled. Aggregate size, pore water velocity, and solution concentration affect the degree of nonequilibrium (Nkedi-Kizza et al., 1983). The governing trans-

port equation for physical nonequilibrium transport of a sorbing solute was formulated by van Genuchten and Wierenga (1976) as follows:

$$\begin{aligned} \theta_m \frac{\partial c_m}{\partial t} + \rho f_p \frac{\partial s_m}{\partial t} + \theta_{im} \frac{\partial s_{im}}{\partial t} + \rho(1 - f_p) \frac{\partial s_{im}}{\partial t} &= \theta_m D \frac{\partial^2 c_m}{\partial x^2} \\ - \theta_m v_m \frac{\partial c_m}{\partial x} \rho(1 - f_p) \frac{\partial s_{im}}{\partial t} + \theta_{im} \frac{\partial c_{im}}{\partial t} &= \alpha_p (c_m - c_{im}) \end{aligned} \quad [9]$$

where the subscripts m and im refer to the mobile and immobile regions, respectively;  $\alpha_p$  is a first-order mass transfer coefficient ( $\text{d}^{-1}$ ), representing the rate of solute exchange between the mobile and immobile regions; and  $f_p$  is the fraction of sorption sites in contact with mobile water. In the case of linear sorption (i.e.,  $n_{Cd} = 1$  in Eq. [1]), Eq. [9] can be solved analytically and used to optimize one or several of the parameters in the transport model (Toride et al., 1995; Šimůnek et al., 1999).

Another formulation for nonequilibrium transport of a sorbing solute was proposed by Selim et al. (1976). Nonequilibrium in their case was assumed to be caused by the kinetics of chemical reactions between the soil solution and the solid phase of the soil. A first-order kinetic rate equation, applicable to heterogeneous ion exchange, was combined with Eq. [8] to obtain the chemical nonequilibrium model. The conceptual model of Selim et al. (1976) divides the exchange sites of the solid soil phase into two domains: Type 1 sites that are in equilibrium with the sorbing solute, and Type 2 sites that are subject to kinetic sorption. For nonlinear Freundlich sorption (Eq. [1]), the nonequilibrium transport equation becomes (Šimůnek et al., 1998):

$$\begin{aligned} \frac{\partial \theta R c}{\partial t} &= \theta D \frac{\partial^2 c}{\partial x^2} - J_w \frac{\partial c}{\partial x} - \alpha_c \rho [(1 - f_c) k c^{n_{Cd}} - s] \\ \frac{\partial s}{\partial t} &= \alpha_c [(1 - f_c) k c^{n_{Cd}} - s] \\ R &= 1 + f_c \frac{\rho}{\theta} n_{Cd} k c^{n_{Cd}-1} \end{aligned} \quad [10]$$

where  $f_c$  is the fraction of equilibrium sites and  $\alpha_c$  a first-order kinetic rate coefficient ( $\text{d}^{-1}$ ). Sorption here is assumed to be nonlinear on both Type 1 and Type 2 sites. We used in this study the numerical solution of Eq. [10] coupled with nonlinear optimization as provided by the HYDRUS-1D code (Šimůnek et al., 1998) to optimize the sorption constant, the Freundlich exponent ( $n_{Cd}$ ), the rate coefficient ( $\alpha_c$ ), and the fraction of equilibrium sites ( $f_c$ ).

## Soil

For the batch and column experiments we used sandy soil (sandy type Humod; Soil Survey Staff, 1998) samples taken from different horizons of a Spodosol profile located at the Kattenbos experimental site (Lommel, Belgium). The profile, situated in the vicinity of non-ferrous industry, is contaminated by atmospheric deposition with heavy metals (Cd, Pb, Zn, and Cu). The (historical) Cd contamination consisted mainly of CdO, which is shown to be readily soluble under acidifying conditions (Smolders, unpublished data, 1999). The soil at the experimental site is moderately contaminated as compared with the contamination at the industrial site itself (i.e., up to  $30 \text{ mg kg}^{-1}$ ). The Cd concentration is representative for the diffuse pollution of the area. The studied Spodosols represent

**Table 1. Properties of the five soil horizons used in the experiments (values represent means of three replicates).**

Horizon	Cd	Zn	pH	CEC <sup>†</sup>	OC <sup>‡</sup>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Sand <sup>§</sup>	Silt <sup>§</sup>	Clay <sup>§</sup>
	— mg kg <sup>-1</sup> —			mmol <sub>c</sub> kg <sup>-1</sup>	%					
A	1.70	69.7	3.7	26.6	3.66	0.20	0.64	94.7	0.28	0.12
E	1.07	5.9	3.9	12.3	0.78	0.09	0.55	92.0	0.38	0.17
Bh	1.93	18.2	3.7	96.7	3.03	1.19	2.32	96.7	1.04	1.11
Bh/C	1.03	15.0	4.4	15.3	0.93	0.68	1.76	96.2	0.17	1.33
C	0.80	12.0	4.6	8.0	0.20	0.57	1.53	98.2	0.33	0.24

<sup>†</sup> Cation exchange capacity.

<sup>‡</sup> Organic carbon content.

<sup>§</sup> Sand (particle size  $\geq 50 \mu\text{m}$ ); silt ( $2 \leq 50 \mu\text{m}$ ); clay (particle size  $< 2 \mu\text{m}$ ).

about 40% of the contaminated area. Table 1 summarizes the main characteristics of the five distinct soil horizons: a humus A horizon, a eluvial E horizon, a Spodic Bh horizon, a transitional Bh/C horizon, and a C horizon (Seuntjens et al., 1999a). Disturbed soil samples were taken from each horizon. The samples were dried at 105°C and crushed with an agate mill before determination of total metal concentration. Total concentrations of Cd, Zn, Al, and Fe were determined using an inductively coupled plasma-atomic emission spectrometer (ICP-AES) after digestion with HNO<sub>3</sub>-HCl-H<sub>3</sub>PO<sub>4</sub>-HBF<sub>4</sub>-HF in a microwave oven. The remaining analyses were performed on air-dried soil. The soil pH was measured in a 1:5 (v/v) suspension of soil in water (pH H<sub>2</sub>O). Total organic carbon was analyzed using a total organic carbon analyzer with infrared spectrometer after combustion in a furnace at 500°C (total carbon) and acidification (total inorganic carbon). The cation exchange capacity (CEC) was determined using BaCl<sub>2</sub> according to an experimental procedure adapted from Gilman (1979).

### Batch Experiments

Upon completing the transport experiments, soil samples were taken from the E and Bh columns to determine the sorption isotherms. For the Bh/C horizon, four field soil samples were taken surrounding the location where the column was sampled. After homogenization, 2 g of air-dry soil was equilibrated with seven different Cd concentrations (5, 50, 100, 250, 500, 750, and 1000  $\mu\text{g L}^{-1}$ ) prepared in a 1:10 (v/v) suspension of soil in 0.001 M CaCl<sub>2</sub>. The suspension was shaken head-over-end for 24 h to ensure equilibrium between soil and solution. After separation of the solute using a 15-min centrifuging at 10 000  $\times g$ , the pH was measured in the supernatant. Concentrations of Cd, Ca, and Zn were measured in the acidified (2% HNO<sub>3</sub>) supernatant using an inductively coupled plasma-atomic emission spectrometer (ICP-AES). Three replicate samples were obtained by repeating the same procedure. The amount of Cd sorbed was calculated from the difference between the initial concentration of the solution and the concentration after equilibration with the soil, divided by the soil to solution ratio.

**Table 2. Summary of the transport experiments.**

Horizon	$L^{\dagger}$	$q$	$\theta$	$v_o^{\ddagger}$	$\rho$	pH	Cl <sup>-</sup> /NO <sub>3</sub> <sup>-</sup> <sup>§</sup>		Cd <sup>III</sup> <sup>§</sup>	
							$c_o$	$T_o$	$c_o$	$T_o$
	cm	cm d <sup>-1</sup>	cm <sup>3</sup> cm <sup>-3</sup>	cm d <sup>-1</sup>	g cm <sup>-3</sup>		mol L <sup>-1</sup>	d	mol L <sup>-1</sup>	d
E	9	32.9	0.26	127	1.59	3.85	0.02	0.017	4.46	0.011
Bh	8	31.7	0.39	81	1.30	3.93	0.02	0.017	4.46	0.011
Bh/C	10.5	100.7	0.36	280	1.43	4.65	0.05	0.0079	4.95	0.0039
Bh/C	10.5	11.4	0.25	46	1.43	4.75	0.05	0.044	4.95	0.026

<sup>†</sup> Length of the soil column.

<sup>‡</sup>  $v_o = q/\theta$ ; the average pore water velocity.

<sup>§</sup>  $c_o$ ,  $T_o$ : input concentration and time pulse, respectively (Cl<sup>-</sup>/NO<sub>3</sub><sup>-</sup> = nonsorbing solute, Cd<sup>III</sup> = sorbing solute).

### Displacement Experiments

In the field, 0.12-m-long and 0.056-m-diam. acrylic sampling cores with sharpened edges were driven into the soil to obtain undisturbed soil samples from the E, Bh, and Bh/C horizons. The soil cores were capped and transferred to the laboratory where they were placed on a porous glass filter (pore size 16  $\mu\text{m}$ ). A 0.001 M CaCl<sub>2</sub> solution was applied at the top boundary at a constant flux using an adjustable-speed peristaltic pump. A rotating lid ensured a homogeneous distribution of the solute at the top of the column. The pH of the solution was adjusted to the pH of the particular soil horizon by adding small amounts of HNO<sub>3</sub> (see Table 2). The resulting ionic strength of the applied solution depended on the desired pH and varied between 0.030 and 0.031 M. In order to establish steady-state unsaturated flow in the soil column, a constant negative pressure head was maintained below the glass filter using a vacuum pump with adjustable pressure. General conditions of the displacement experiments are given in Table 2. The experiments in the Bh/C column were conducted consecutively at two different flux densities to evaluate the effect of water flux on Cd transport.

A fraction collector allowed the collection of effluent samples from two columns simultaneously every 20 min. Indigenous Cd, Ca, and Cl concentrations and the pH of the effluent were measured. When the pH reached a constant value, a pulse of <sup>111</sup>Cd stable isotope (dissolved in a 1% HNO<sub>3</sub> solution, pH 1) in a 0.001 M CaCl<sub>2</sub> background solution was added to the soil column and leached with 0.001 M CaCl<sub>2</sub>. To adjust the pH to the pH of the particular soil horizon, NaOH was added to the solution. This resulted in a <sup>111</sup>Cd background solution of 0.05 M NaNO<sub>3</sub> and 0.001 M CaCl<sub>2</sub>. Indigenous Cd and <sup>111</sup>Cd isotope concentrations were determined simultaneously in the collected sample fractions using an inductively coupled plasma-mass spectrometer (ICP-MS). Details of the calibration, the analytical analysis of the different Cd isotopes, and the accompanying uncertainty analysis can be found in Tirez et al. (1999).

A displacement experiment with a nonsorbing solute was next conducted on the same soil columns to obtain physical transport parameters. A single pulse of 0.02 M CaCl<sub>2</sub> (for the

**Table 3. Nonlinear least-squares fit of the Freundlich parameters. The traditional Freundlich (Eq. [1]), two-species Freundlich (2SF, Eq. [2]), and three-species Freundlich (3SF, Eq. [3]) isotherms were used in the analysis.**

Horizon	Freundlich (Eq. [1])			2SF (Eq. [2])			3SF (Eq. [3])		
	$k_f$	$n_{Cd}$	$R^2$	$k_{2SF}$	$n_{Cd}$	$R^2$	$k_{3SF}$	$n_{Cd}$	$R^2$
	$mg^{(1-n)} L^n kg^{-1}$			$mg^{(1-n)} L^n kg^{-1}$			$mol^{(1-n)} L^n kg^{-1}$		
A	16.7	0.31	0.83	0.040	0.77	0.98	$2.33 \times 10^{-4}$	0.88	0.98
E	7.2	0.75	0.99	0.104	0.80	1.00	$3.76 \times 10^{-4}$	0.83	1.00
Bh	26.1	0.86	0.98	0.152	0.86	1.00	$7.58 \times 10^{-4}$	0.87	1.00
Bh/C	5.8	0.77	0.98	0.038	0.75	0.98	$3.00 \times 10^{-5}$	0.74	0.98
C	1.5	0.53	0.82	0.039	0.75	0.63	$8.53 \times 10^{-6}$	0.65	0.94
All horizons	no convergence			0.046	0.94	0.86	$1.68 \times 10^{-4}$	0.86	0.82

E and Bh columns) or 0.05 M NaNO<sub>3</sub> (for the Bh/C columns) was applied at the top of the soil columns. Effluent conductivity was continuously monitored at the outlet of the soil columns using a flow-through conductivity electrode connected

to a conductivity meter and a personal computer for automatic data collection.

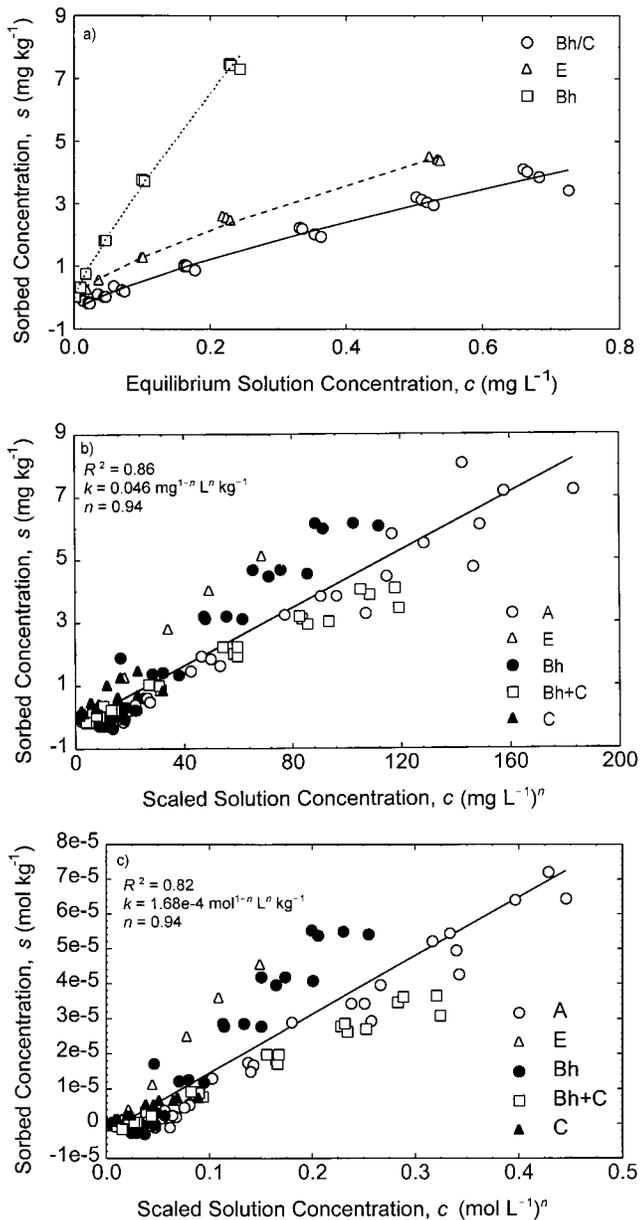
**RESULTS AND DISCUSSION**

**Sorption Isotherms**

Sorption constants and exponents of the Freundlich isotherm (Eq. [1]), the two-species Freundlich isotherm (2SF, Eq. [2]), and the three-species Freundlich equation (3SF, Eq. [3]) were optimized using a nonlinear least-squares procedure taken from the STATISTICA software package (Statsoft, 1996). Because the Bh/C soil sample contained a considerable amount of indigenous Cd, the intercept of the Freundlich isotherm was fitted as well. During optimization, the exponents  $m$  in Eq. [2] and  $m$  and  $n_{Ca}$  in Eq. [3] were fixed at values obtained for similar soils by van der Zee and van Riemsdijk (1987) (i.e.,  $m = -0.5$ ) and Temminghoff et al. (1995) (i.e.,  $m = -0.69$  and  $n_{Ca} = -0.34$ ), respectively. Results of the optimizations are given in Table 3. The Freundlich isotherm (Eq. [1]) had  $k_f$  values ranging from 1.5  $mg^{(1-n)} L^n kg^{-1}$  for the C horizon to 26.1  $mg^{(1-n)} L^n kg^{-1}$  for the humus Bh horizon. The isotherms were strongly nonlinear with exponents  $n_{Cd}$  between 0.31 and 0.86. The low  $n_{Cd}$  values for the A and C horizons were partly due to a poor fit between measured and optimized data. Figure 1a presents the Freundlich isotherms for the E, Bh, and Bh/C horizons (i.e., those used in the displacement experiments). The negative intercept of the Bh/C isotherm (i.e.,  $-0.45 mg kg^{-1}$ ) indicates desorption at low concentrations.

The optimized Freundlich exponents  $n_{Cd}$  of the 2SF model (Eq. [2]) ranged from 0.75 in the E horizon to 0.86 in the Bh horizon. Except for the humus Bh horizon,  $n_{Cd}$  values were considerably smaller than the value of 0.85 obtained by van der Zee and van Riemsdijk (1987). The A horizon produced a significantly higher coefficient of determination ( $R^2$ ) for the 2SF isotherm as compared with the Freundlich isotherm, while  $R^2$  for the C horizon was much lower (Table 3). These results suggest that differences in soil organic matter and pH explain the variance between the different Freundlich isotherms for the A horizon, but not for the C horizon. The low  $R^2$  for the C horizon indicates that the variance of the sorption constant cannot be adequately explained by variations in soil organic matter and pH.

The optimized sorption parameter  $k_{3SF}$  of the three-species Freundlich isotherm varied from  $8.53 \times 10^{-6}$  for the C horizon to  $7.58 \times 10^{-3} mol^{(1-n)} L^n kg^{-1}$  for the



**Fig. 1. Cadmium sorption isotherms: (a) Freundlich isotherm for three different horizons, (b) field-scale averaged two-species Freundlich isotherm, and (c) field-scale averaged three-species Freundlich isotherm.**

**Table 4.** Nonlinear least-squares fits of the parameters  $v_m$ ,  $D_m$ ,  $\theta_m$ , and  $\alpha_p$  in the two-region model (TRM) and the parameters  $v$  and  $D$  in the convection-dispersion model (CDE) (values in brackets are standard errors of estimate).

Horizon	CDE				TRM						
	$v$	$D$	$\lambda^\dagger$	$R^2$	$v_m^\ddagger$	$D_m^\ddagger$	$\lambda_m^\S$	$\theta_m/\theta$	$\omega$	$\alpha_p^\S$	$R^2$
	cm d <sup>-1</sup>	cm <sup>2</sup> d <sup>-1</sup>	cm		cm d <sup>-1</sup>	cm <sup>2</sup> d <sup>-1</sup>	cm			d <sup>-1</sup>	
E	134 (1.45)	23.3 (2.23)	0.17	0.96	126 (1.49)	6.7 (1.97)	0.06	0.84 (0.019)	0.94 (0.25)	2.90	0.99
Bh	99 (0.46)	19.3 (0.67)	0.19	0.99	98 (0.55)	1.9 (9.5)	0.03	0.65 (0.23)	5.6 (4.5)	2.54	0.99
Bh/C	349 (2.98)	111 (6.48)	0.32	0.94	308 (2.42)	28 (2.21)	0.12	0.78 (0.006)	0.78 (0.047)	7.78	0.99
Bh/C	31 (0.20)	11.6 (0.45)	0.37	0.96	29 (0.12)	3.7 (0.21)	0.16	0.79 (0.006)	1.02 (0.065)	0.64	0.99

$^\dagger \lambda = D/v$ ;  $\lambda_m = D_m/v_m$ .

$^\ddagger v_m = v\theta/\theta_m$ ,  $D_m = D\theta/\theta_m$ .

$^\S \alpha_p = \omega\theta v/L$ .

Bh horizon. This large variation in sorption constants between soil layers indicates that Ca is presumably not the only competing metal ion for the same sorption sites. Based on the coefficients of determination, the 3SF model describes sorption of Cd in the C horizon significantly better than the 2SF model.

Isotherm data from all horizons (A, E, Bh, Bh/C, and C) were pooled in order to derive *field-scale* averaged 2SF and 3SF isotherms. The average 2SF and 3SF isotherms are shown in Fig. 1b and 1c, respectively. Results of the optimization suggest that 86% of the variance of the sorption constant  $k_{2SF}$  between samples from different layers is explained by the organic matter content and the pH. The average 3SF model, which additionally includes Ca activity, ionic strength, and choride complexation, does not seem to predict sorbed concentrations better than the average 2SF model. The value of 0.046 for the modified 2SF sorption constant  $k_{2SF}$  corresponds remarkably well with the modified Freundlich constant ( $k_{2SF} = 0.048 \text{ mg}^{(1-n)} \text{ L}^n \text{ kg}^{-1}$ ) derived by van der Zee and van Riemsdijk (1987). Optimizing  $k_{3SF}$  and  $n_{Cd}$  of the modified 3SF equation to isotherm data from all horizons resulted in a modified  $k_{3SF}$  of  $10^{-3.77} \text{ mol}^{(1-n)} \text{ L}^n \text{ kg}^{-1}$  and in a  $n_{Cd}$  value of 0.86. The modified 3SF constants are close to the values obtained by Temminghoff et al. (1995), assuming that the organic carbon content in our soil is equal to 1%. Depth averages of organic carbon content in our soil (i.e., OC = 1.01%) indicate that this assumption is indeed valid. The results show that sorption of cadmium in our layered sandy soil can be reasonably well approximated by modified isotherms valid for the entire soil profile.

## Transport Experiments

### Nonreactive Transport

The parameters  $v$  and  $D$  of the convection–dispersion model (CDE) (Eq. [8] with  $\partial s/\partial t = 0$ ), as well as the parameters  $v_m$ ,  $D_m$ , and  $\theta_m$  of the two-region model (TRM) (Eq. [9], with  $\partial s_m/\partial t = 0$  and  $\partial s_{im}/\partial t = 0$ ), were optimized using the chloride breakthrough data for the E and Bh horizons, and the nitrate breakthrough data for the Bh/C horizon. The optimized CDE and TRM parameters obtained using the CXTFIT curve-fitting program (Toride et al., 1995) are given in Table 4. The dispersivity ( $\lambda$ ) calculated from the CDE parameters  $v$

and  $D$  for the Bh/C horizon was somewhat larger for the lower water content experiment. This is consistent with observations by Biggar and Nielsen (1960), who suggested that the flow path should become more tortuous when the soil water content decreases, thus leading to higher dispersivities. Quadruplicate displacement experiments at three different fluxes for four different horizons of the same soil confirmed this inverse relationship between the water content and dispersivity (results not further shown here).

Figure 2 shows that the CDE model slightly underestimated the peak concentrations and poorly described the tailing parts of the breakthrough curves for the E and Bh/C horizons, while the TRM model described both the peak and the tailing well. Transport in the Bh horizon was equally well described using the CDE and TRM models. Relatively large values of the dimensionless mass transfer coefficient ( $\omega$ ) (typically larger than 10) are indicative of local equilibrium during transport, in which case Eq. [4] should be the appropriate transport model. The optimized  $\omega$  values shown in Table 4 are smaller than or equal to 1, except for the Bh horizon. This indicates a significant degree of nonequilibrium in the E and Bh/C horizons for the imposed water fluxes. The relative mobile water contents ( $\theta_m/\theta$ ) ranged from 0.65 to 0.84. These values are comparable with those obtained in other studies on sandy soils (Gaudet et al., 1977; Vanclooster et al., 1993). Calculated mass transfer coefficients ( $\alpha_p$ ) increased with increasing pore water velocity ( $v$ ), which confirms findings by Nkedi-Kizza et al. (1983), Reedy et al. (1996), and Pang and Close (1999), among others. A higher pore water velocity or, equivalently, a shorter solute residence time, promotes incomplete mixing of solutes between mobile and stagnant pore water, and a larger diffusive mass transfer rate coefficient  $\alpha_p$ .

In the following sections we will discuss Cd transport for the same columns and the same boundary conditions as the above tracer experiments. The  $v$  and  $D$  parameters, optimized using the (macroscopic) CDE model, will be used to predict breakthrough of the sorbing solute. Since physical nonequilibrium conditions prevailed in the E and Bh/C horizons,  $D$  optimized using the CDE model is considered to be an effective model parameter for these columns. The effective dispersion coefficient lumps two processes (e.g., Valocchi, 1985):

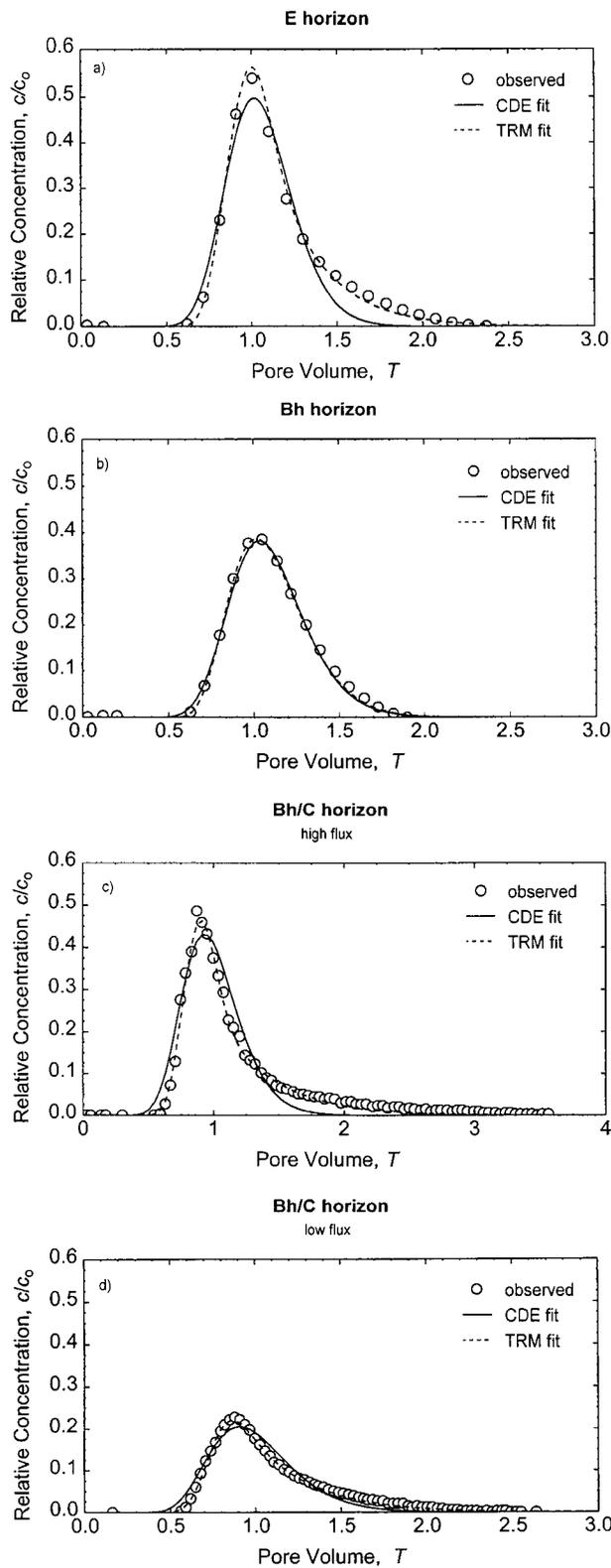


Fig. 2. Observed chloride (E, Bh) and nitrate (Bh/C) breakthrough data and fitted curves using the convection–dispersion (CDE) and two-region (TRM) models for (a) the E horizon, (b) the Bh horizon, (c) the Bh/C horizon with high flux, and (d) the Bh/C horizon with low flux.

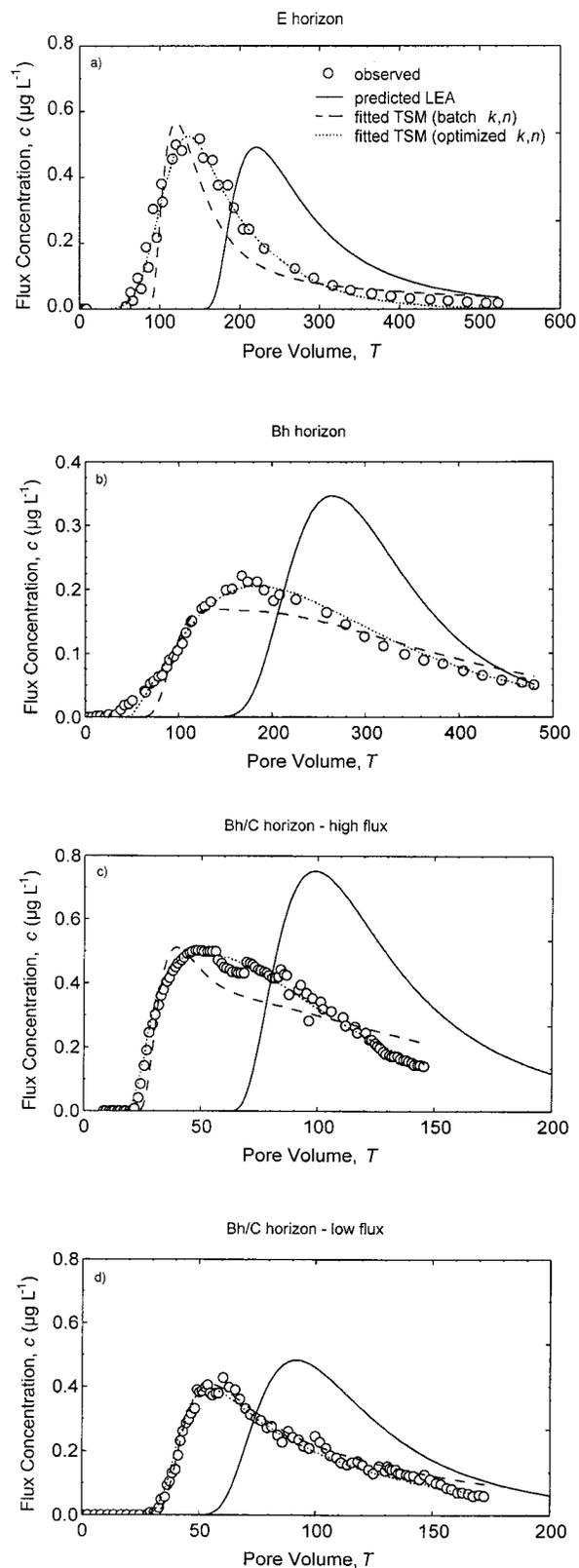


Fig. 3. Non-aged  $^{111}\text{Cd}$  breakthrough data for (a) the E horizon, (b) the Bh horizon, (c) the Bh/C horizon with high flux, and (d) the Bh/C horizon with low flux. Curves represent predictions of  $^{111}\text{Cd}$  concentrations using the convection–dispersion (CDE) model with independently determined parameters (predicted local equilibrium [LEA]), using the optimized two-site model (TSM) with  $k$  and  $n$  determined from batch experiments (fitted two-site model [TSM], batch  $k$  and  $n$ ), and using the optimized TSM model with  $k$  and  $n$  also fitted (fitted TSM, optimized  $k$  and  $n$ ).

dispersion owing to variations in the pore water velocity ( $v_m$ ) and additional dispersion due to limited mass transfer between stagnant and mobile water phases.

### Equilibrium Cadmium Transport

Measured breakthrough curves (BTCs) of  $^{111}\text{Cd}$  are shown in Fig. 3. The BTCs are asymmetrical, displaying a relatively sharp breakthrough front and prolonged tailing. Recovery rates calculated from observed  $^{111}\text{Cd}$  concentrations in the column effluent were 96, 80, 66, and 72% for the E and Bh horizons, and the Bh/C horizons at the high and low fluxes, respectively. Given the incomplete observed effluent curves for columns Bh and Bh/C, the recovery percentages indicate that the  $^{111}\text{Cd}$  isotope probably sorbs reversibly.

Independent predictions of the  $^{111}\text{Cd}$  breakthrough curves (denoted as predicted local equilibrium [LEA] in Fig. 3) were made using the dispersivity  $\lambda$  obtained from the nonreactive tracer experiments and  $k_f$  and  $n_{\text{Cd}}$  parameters derived from batch data using the Freundlich isotherm (Eq. [1]). The calculations were performed using the HYDRUS-1D code (Šimůnek et al., 1998). As explained before, physical nonequilibrium conditions existed in the E and Bh/C horizons. Therefore, our calculations assume chemical equilibrium and physical nonequilibrium in the E and Bh/C horizons, and chemical and physical equilibrium in the Bh horizon.

As shown in Fig. 3, the chemical equilibrium model generally failed to predict the observed breakthrough data of the  $^{111}\text{Cd}$  isotope. The mean breakthrough time was substantially overestimated, while spreading of the breakthrough curve was underestimated. The  $^{111}\text{Cd}$  isotope seemed to travel much faster than predicted with the equilibrium model. The rather severe deviations between the observed and predicted Cd breakthrough curve are presumably caused by (i) overestimation of retardation using the batch sorption parameters and/or (ii) inability of the chemical to reach equilibrium with the solid phase during transport through the soil. Two mechanisms may explain this observed nonequilibrium (van Genuchten and Cleary, 1982). Chemical nonequilibrium can be due to kinetic sorption (i.e., the sorption reaction is too slow compared with the transport velocity to ensure chemical equilibrium between sorbate and sorbent). Second, physical constraints during transport may prevent a chemical from reaching the exchange sites in the soil. The diffusion rate of the chemical from the mobile water fraction to the stagnant water surrounding the sorption sites is then slow compared with the transport velocity in the mobile water fraction. Real chemical kinetic nonequilibrium may explain the fast breakthrough in the Bh horizon, because no physical nonequilibrium was demonstrated by the displacement experiment using the nonsorbing tracer. In the other soil columns, both types of nonequilibrium probably were operative at the same time. The equilibrium model predicted  $^{111}\text{Cd}$  breakthrough at the low flux in the Bh/C horizon relatively well, although still relatively fast breakthrough and tailing occurred.

Leaching of indigenous Cd is presented in Fig. 4.

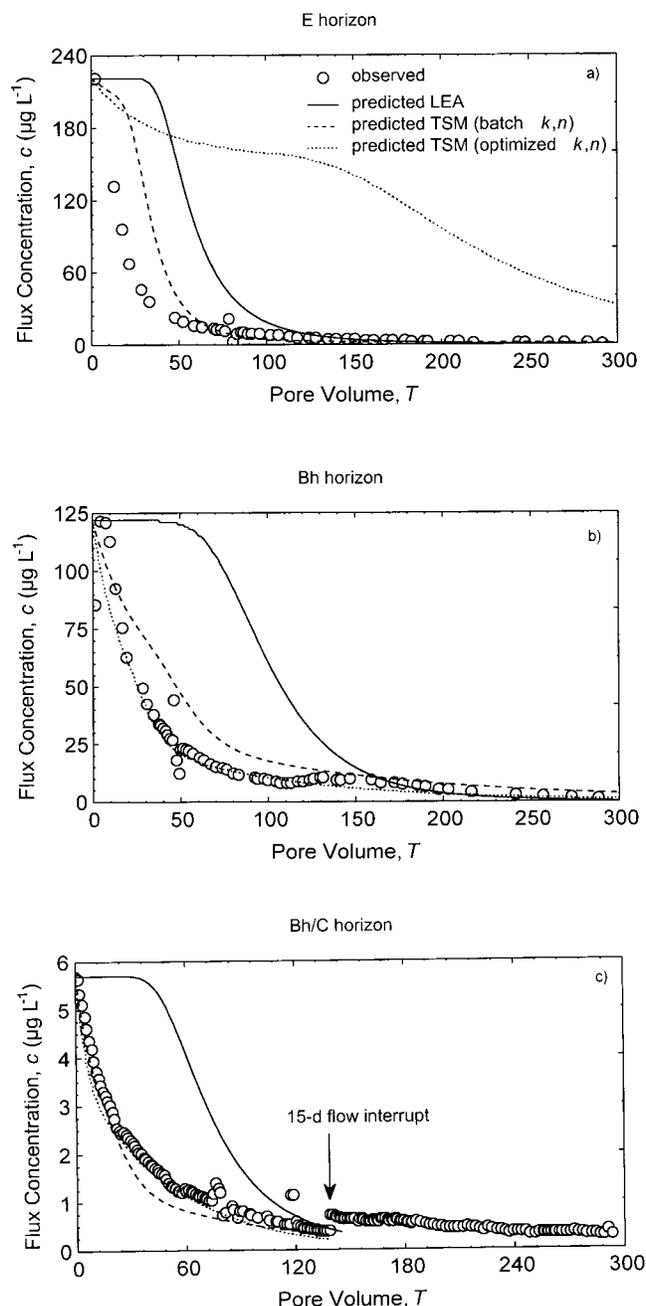


Fig. 4. Indigenous aged Cd breakthrough data for (a) the E horizon, (b) the Bh horizon, and (c) the Bh/C horizon with high flux. Curves represent predictions of Cd concentrations using the convection-dispersion (CDE) model with independently determined parameters (predicted local equilibrium [LEA]), using the optimized two-site model (TSM) with  $k$  and  $n$  determined from batch experiments (predicted TSM, batch  $k$  and  $n$ ), and using the optimized TSM model with  $k$  and  $n$  also fitted (predicted TSM, optimized  $k$  and  $n$ ). The TSM model parameters were optimized using the  $^{111}\text{Cd}$  breakthrough curve.

The effluent curves initially show a sharp decrease in concentration and a more gradual decrease toward the end of the experiments. The increase in Cd concentrations between 50 and 100 pore volumes is due to increased ionic strength resulting from the  $^{111}\text{Cd}$  tracer pulse (0.05 M  $\text{NaNO}_3$ , 0.001 M  $\text{CaCl}_2$  background). The increase is followed by sharp decrease due to increased

**Table 5. Two-parameter optimizations of the nonequilibrium parameters  $\alpha_c$  and  $\beta_c$  using the two-site kinetic model and independently measured parameters  $k_f$  and  $n_{Cd}$  obtained from the batch experiments (values between parentheses are standard errors of estimate).**

Horizon	Fixed		$^{111}\text{Cd}$			Indigenous Cd		
	$k_f$	$n_{Cd}$	$f_c$	$\alpha_c$	$R^2$	$f_c$	$\alpha_c$	$R^2$
	$\mu\text{g}^{(1-n)} \text{L}^n \text{kg}^{-1}$			$\text{d}^{-1}$			$\text{d}^{-1}$	
E	40.5 (6.7)	0.75 (0.03)	0.60 (0.010)	0.08 (0.014)	0.81	0.34 (0.005)	0.28 (0.014)	0.99
Bh	68.6 (7.5)	0.86 (0.02)	0.43 (0.013)	0.19 (0.010)	0.91	0.37 (0.008)	0.15 (0.014)	0.94
Bh/C-high flux	28.3 (9.5)	0.77 (0.05)	0.41 (0.007)	0.90 (0.030)	0.85	0.48 (0.004)	1.21 (0.040)	0.96
Bh/C-low flux	28.3 (9.5)	0.77 (0.05)	0.63 (0.005)	0.08 (0.002)	0.98			

sorption of Cd and release of Na. This phenomenon is, however, of short duration (except for column Bh) and does not seem to affect leaching of indigenous Cd. Recovery percentages, calculated from the ratio of the cumulative Cd mass in the column effluent and the initial total Cd mass in the soil columns, were 30, 38, 54, and 87% for the E, Bh, and high-flux and low-flux Bh/C soil columns, respectively.

Predictions made using the equilibrium model (i.e., assuming local equilibrium [LEA]) strongly deviated from the observed transport data. The chemical equilibrium model clearly failed to predict the sharp concentration decrease and overestimated the mass leached within the calculated period. Apparently, desorption and/or mass transfer of Cd to the transport flow regions is too slow to assume equilibrium. We note here that the boundary conditions for the low-flux leaching case of column Bh/C were different from those of the other columns. As shown in Fig. 4, the gradual decrease in concentration between 150 and 300 pore volumes (low-flux leaching) is preceded by a sudden increase resulting from a 15-d interrupted flow period between the high- and the low-flux cases in the same column. Therefore, the low-flux experiment cannot be considered as an initial value problem similar to the other columns, and no predictions were made for this case.

### Nonequilibrium Cadmium Transport

From the available observations we could not conclude conclusively whether irreversible sorption or nonequilibrium due to rate-limited diffusion or kinetic sorption was responsible for the low recovery percentages and the overall poor prediction of the Cd breakthrough curves using the equilibrium model. We pointed out earlier that no clear evidence exists in the literature that irreversible Cd fixation occurs in acid sandy soils (Smolders et al., 1999). Therefore, in our calculations below we will assume that nonequilibrium is responsible for deviations between predicted and observed Cd breakthrough curves. Several researchers have demonstrated that actual Cd sorption is instantaneous in well-stirred and sieved soils (e.g., Christensen, 1984a). However, in systems with flowing water, and especially in aggregated or unsaturated soils, the global reaction rate can be limited by the rate at which ions are transported to the exchange sites, even when the actual sorption reaction is instantaneous (Nkedi-Kizza et al., 1984). In the next section we describe Cd transport using the

chemical nonequilibrium transport model (Eq. [10]), which assumes that sorption is reversible, but that the global reaction is not instantaneous at some fraction of the sorption sites.

The fraction of sites  $f_c$  for which sorption is instantaneous, and the first-order kinetic rate coefficient  $\alpha_c$ , were optimized using a numerical solution of Eq. [10] (Šimůnek et al., 1998), while fixing the Freundlich parameters  $k_f$  and  $n_{Cd}$  to the independently measured batch values. Results of the optimization are given in Table 5 for both the  $^{111}\text{Cd}$  isotope and the indigenous Cd. Figure 3 shows that the nonequilibrium model adequately predicts the position of the  $^{111}\text{Cd}$  breakthrough curve. The model, however, failed to correctly describe the early breakthrough data and tailing for the E, Bh, and Bh/C (high flux) columns. Optimizing  $f_c$  and  $\alpha_c$  for the low-flux breakthrough curve for the Bh/C column resulted in an almost perfect prediction of the adsorption front of the BTC, whereas tailing was somewhat overestimated.

The description of the  $^{111}\text{Cd}$  breakthrough curve improved significantly when all four parameters ( $k_f$ ,  $n_{Cd}$ ,  $\alpha_c$ ,  $f_c$ ) in Eq. [10] were optimized. Figure 3 illustrates the close correspondence between model results and experimental data. The optimized parameters are given in Table 6. The optimized sorption constants  $k_f$  from the column experiments were consistently smaller than the  $k_f$  values obtained from the batch experiments (Table 2), whereas the optimized exponents  $n_{Cd}$  were larger than the batch values, except for the Bh horizon. Based on the standard errors of estimate of measured and optimized  $k_f$  and  $n_{Cd}$  parameters, differences between  $k_f$  and  $n_{Cd}$  optimized using the breakthrough data and fitted to the batch data seem to be rather small. Only for the E column did we find that the optimized  $n_{Cd}$  from the column breakthrough data was significantly larger than the batch value. We believe that results of the four-parameter fit for this column are unreliable and should be interpreted with care.

Independent predictions of indigenous Cd leaching using model parameters obtained from the displacement tests with  $^{111}\text{Cd}$  isotope are displayed in Fig. 4. Independent predictions were made using the batch  $k_f$  and  $n_{Cd}$  values and  $f_c$  and  $\alpha_c$  values estimated from the  $^{111}\text{Cd}$  breakthrough curve (Table 5, depicted as predicted two-site model [TSM] batch  $k, n$  in Fig. 4), as well as using all  $k_f$ ,  $n_{Cd}$ ,  $\alpha_c$ , and  $f_c$  parameters fitted to the  $^{111}\text{Cd}$  breakthrough curve (Table 6, depicted as predicted TSM opti-

**Table 6. Four-parameter optimizations of the nonequilibrium parameters  $\alpha_c$  and  $\beta_c$  and sorption parameters  $k_f$  and  $n_{cd}$  using the two-site kinetic model (values between parentheses are standard errors of estimate).**

Horizon	$k_f$ $\mu\text{g}^{(1-n)} \text{L}^n \text{kg}^{-1}$	$n_{cd}$	$f_c$	$\alpha_c$ $\text{d}^{-1}$	$R^2$
E	30.9 (0.83)	1.06 (0.04)	0.69 (0.02)	0.29 (0.04)	0.98
Bh	55.0 (2.5)	0.81 (0.04)	0.40 (0.04)	0.31 (0.04)	0.98
Bh/C-high flux	20.1 (0.17)	0.90 (0.001)	0.44 (0.004)	1.74 (0.04)	0.99
Bh/C-low flux	24.9 (0.49)	0.82 (0.02)	0.62 (0.01)	0.10 (0.008)	0.99

mized  $k, n$  in Fig. 4). A comparison between the observed and as such predicted indigenous Cd leaching should provide evidence whether or not the transport behavior of  $^{111}\text{Cd}$  and indigenous Cd is similar. Fig. 4 shows that leaching of indigenous Cd in the E horizon cannot be described using parameters determined from the  $^{111}\text{Cd}$  isotope. Much better predictions of Cd leaching were obtained using the batch  $k_f$  and  $n_{cd}$  values (two-parameter fit) than when those two parameters were optimized to the  $^{111}\text{Cd}$  breakthrough data (four-parameter fit). This again shows that the four-parameter optimization may yield unreliable results in this case. The results also suggest that transport of  $^{111}\text{Cd}$  in the E column is closer to equilibrium than leaching of indigenous Cd. This is confirmed by the larger fraction of equilibrium sites  $f_c$  for  $^{111}\text{Cd}$  than for indigenous Cd (Table 5). For the Bh and Bh/C horizons, indigenous Cd leaching was described adequately using  $^{111}\text{Cd}$  parameters. No differences between the transport behavior of aged and non-aged Cd in these two layers could be inferred from the available observations.

The kinetic rate coefficient  $\alpha_c$  was smaller at low water fluxes than at large water fluxes. Similar observations of the dependence of the mass transfer rate coefficient on boundary conditions were reported by Gaber et al. (1995) for atrazine. This indicates that diffusion, rather than sorption kinetics, probably limits the transfer from exchange sites to mobile soil water.

## CONCLUSIONS

Sorption and transport of Cd in undisturbed unsaturated soil horizons of a multilayered sandy soil was investigated. Sorption of Cd was nonlinear and could be described well using a Freundlich isotherm. A two-species Freundlich (2SF) isotherm, accounting for the (horizontal) variance of organic matter and pH, improved the prediction of sorption in the humus A horizon, but failed to predict sorption in the deeper C horizon. A three-species Freundlich (3SF) isotherm adequately described sorption in all horizons. The 3SF isotherm predicted sorption in the C horizon better as compared with the 2SF isotherm, thus showing that soil water composition has to be taken into account when estimating sorption of Cd in the deeper soil layers.

Modified 2SF isotherms that accounted for the variability of organic matter and pH in the entire soil profile were found to explain 86% of the variance of sorbed

Cd concentrations. Modifying the 3SF isotherm did not improve the predictions as compared with the 2SF isotherm. Additional experiments at the scale of an entire soil profile are needed to evaluate the usefulness of modified isotherms in predicting transport through layered soil profiles.

Unsaturated conditions during the displacement experiments for the two soil layers (i.e., the eluvial E horizon and the transitional Bh/C horizon) produced physical nonequilibrium. Mobile water fractions were found to be about 80% of the total water content, indicating that 20% of the soil water did not contribute to transport. Physical equilibrium prevailed in the low-permeability humus Bh horizon, which previously had been shown to redistribute solute in the soil profile (Seuntjens et al., 1999b). The mass transfer coefficient  $\alpha_p$  depended on water flux, thus showing that diffusion limited the solute exchange between mobile and stagnant soil water.

The local equilibrium convection–dispersion model failed to describe breakthrough curve of  $^{111}\text{Cd}$  isotope and leaching of indigenous Cd. Parameters optimization using the two-site kinetic nonequilibrium model showed that retardation was somewhat overestimated by the batch parameters, and that the global sorption rate was not instantaneous at about 30 to 60% of the sorption sites. Mass transfer coefficients were found to depend on the water flux, which suggests that diffusion rather than kinetic sorption was responsible for the observed nonequilibrium.

Predictions of Cd leaching using parameters representative for non-aged Cd compared favorably with observed leaching of aged Cd in the humus Bh horizon and the transitional Bh/C horizon. The transport behavior of non-aged and aged Cd hence was about the same in these two layers. Aging seemed to affect the leaching behavior of Cd in the E horizon as shown by a disparity in optimized model parameters between aged and non-aged Cd.

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